GENERATION, SAMPLING AND ANALYSIS OF GB (SARIN) VAPOR FOR INHALATION TOXICOLOGY STUDIES

William T. Muse, Steven J. Anthony, Leonard C. Buettner, Charles L. Crouse, Lee C. Crouse, Robert J. Mioduszewski, and Sandra A. Thomson

USA Soldier Biological Chemical Command
Edgewood Chemical Biological Center
ATTN: AMSSB-RRT-TT
5183 Blackhawk Road
Aberdeen Proving Ground, MD 21010-5424 USA

ABSTRACT

This study tested and optimized various methodologies to generate, sample and characterize GB test atmospheres in an inhalation chamber. A syringe drive spray atomization system was used for GB vapor generation. Stable GB test atmospheres (0.5 – 50 mg/m^3) were generated over different duration's (60, 240, 360 min) and sampled with solvent bubblers as well as an automated solid sorbent sampling system. Concentrations derived from each sampling method were compared against each other and statistically evaluated. A paired t-test showed no statistical difference between the two methods at the 95% confidence interval. Future applications include the ability to generate and monitor GB levels approaching the TLV-TWA of 0.0001 mg/m^3.

1. INTRODUCTION

Sampling for organic vapors in air has traditionally been performed using solvent bubblers. In this methodology, organic vapors are typically drawn through a glass collection tube or "bubbler" containing an appropriate solvent.[1] The dissolution of the organic vapor with the solvent traps the vapor within the bubbler. Once sampling is completed, the solvent containing the absorbed organic is diluted to a known volume and quantitated, typically through gas chromatographic analysis. Problems with bubbler usage include handling, dilution of analyte, time consumption, and sample flow rate correction particularly as a result of solvent evaporation.

The development of a solid sorbent tube sampler followed by thermal desorption, has become a more recently accepted methodology for the analysis of organic vapors in air. This technology has provided near real time monitoring for occupational exposure to chemical warfare agents since 1992.[2] A solid absorbent, such as Tenax TA is packed into a small glass sampling tube. As the test atmosphere is sampled through the tube, organic vapors are adsorbed onto the resin. At the completion of sampling, the trapped organics are thermally desorbed directly onto a gas chromatograph for quantitation. Advantages

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
00 JAN 2002	**N/A**	**-**

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
Generation, Sampling And Analysis Of Gb (Sarin) Vapor For Inhalation Toxicology Studies	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **USA Soldier Biological Chemical Command Edgewood Chemical Biological Center ATTN: AMSSB-RRT-TT 5183 Blackhawk Road Aberdeen Proving Ground, MD 21010-5424 USA**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release, distribution unlimited

13. SUPPLEMENTARY NOTES
This article is from ADA409494 Proceedings of the 2001 ECBC Scientific Conference on Chemical and Biological Defense Research, 6-8 March , Marriott's Hunt Valley Inn, Hunt Valley, MD., The original document contains color images.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			
unclassified	**unclassified**	**unclassified**	**UU**	**12**	

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

of this method over bubblers include, higher sampling flow, ease of use, automation, no solvent dilution, and increased sensitivity.

Previous inhalation studies (Cullumbine et al,[3] Barrett,[4] and Callaway and Blackburn[5]) have traditionally used bubblers to quantitate for GB vapor to establish lethality (LCt_{50}) on different animal species. A recent study by Mioduszewski et al.,[6] has repeated some of these previous GB vapor concentrations but varied exposure time to determine whether Haber's Rule (Concentration x Time = Constant) applies in predicting GB lethality. To compare previous GB toxicity studies with the Mioduszewksi study, bubbler samples were drawn to determine the chamber concentration. At the same time, an automated solid-sorbent tube system sampled the chamber concurrently with the bubblers. A statistical comparison of the data from the two sampling methods was conducted. A favorable comparison between the two sampling techniques would place increased confidence on the solid-sorbent tube methodology, particularly when conducting future GB vapor toxicity studies below the practical limits for bubbler sampling.

This study also tested the performance of a syringe drive coupled with a modified spray-atomizer to determine it's effective range and capability to generate long term stable GB vapor concentrations in an inhalation chamber.

2. MATERIALS AND METHODS

2.1 CHEMICALS

Chemical agent standard analytical reagent material (CASARM)-grade Sarin (GB) (lot # GB-U-6814-CTF-N (GB2035) was verified as 97.2 $\pm$ 0.2 wt % (as determined by quantitative NMR ^{31}P) in samples obtained from USAECBC and stored in sealed ampules containing nitrogen. Ampules were opened as needed to prepare external standards or to be used as neat agent for vapor dissemination. All external standards for GB vapor quantitation were prepared on a daily basis. Triethylphosphate (99.9% purity), obtained from Aldrich Chemicals, Milwaukee, WI, was used as the internal standard for the GB purity assay.

The majority of impurities in the CASARM GB consisted of 0.2% o,o'-diisopropyl methylphosphonate (DIMP), 0.2 % methylphosphonic difluoride (DF), 0.3% methylphosphonofluoridic acid (Fluor Acid), and 0.3% excess HF/F ion. Impurity percentages were based on mole ratios from acid-base titration.

2.2 GB TEST ATMOSPHERE, OVERVIEW

GB test atmospheres were generated by dispensing liquid GB into a vapor generation system, which in turn was connected to the inlet of a dynamic flow inhalation chamber. The GB vapor was monitored in the chamber with a variety of sampling techniques, including bubbler, sorbent tube and a continuous phosphorus analyzer (Fig 1). Concentrations derived from the bubbler and sorbent tube were compared against each other and statistically evaluated. The phosphorus analyzer was used primarily to monitor the chamber vapor profile, that is the rise, equilibration and fall of the GB vapor concentration during a chamber run. Testing and evaluation ranged from 2 - 7 mg/m^3 GB to compare the bubbler vs. sorbent tube. Concentrations from 0.5 - 50 mg/m^3 were run to test the performance of the syringe drive/spray atomizer.

2.3 GENERATION SYSTEM

The generation system consisted of a syringe drive and spray atomization system located on top of the inhalation chamber (chamber inlet). The system was confined within a stainless steel generator box (23"l x 14"w x 18"h) which was maintained under negative pressure (0.25" H_2O). A Plexiglas door at the front of the box allowed for syringe loading and syringe drive adjustments during set-up operations.

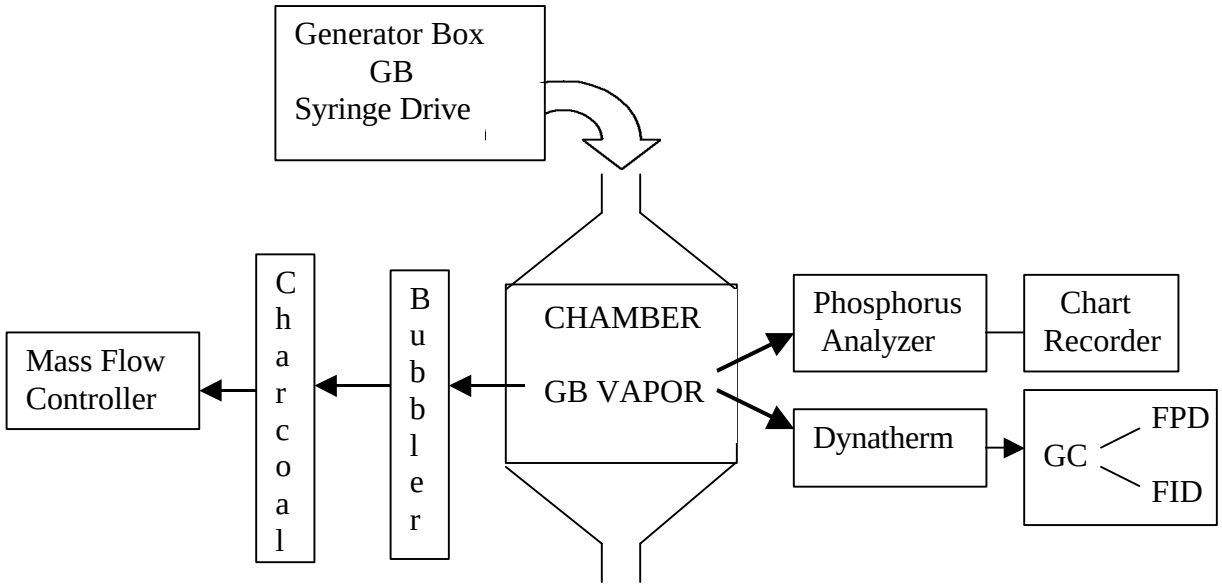


Figure 1. Schematic for GB inhalation chamber and monitoring systems.

2.3.1 SYRINGE DRIVE/SPRAY ATOMIZATION SYSTEM

Prior to chamber operation, the liquid GB was drawn into a gas-tight syringe (Hamilton, Reno, NV), transported to the generator box, then mounted onto a variable rate syringe drive (Model 22, Harvard Apparatus Inc., South Natick, MA). Once activated, the syringe drive delivered a constant flowrate of GB (ul/min) through a flexible plastic line (~ 8") into a spray atomization system (Spray Atomization Nozzle 1/4 J SS, Spraying Systems Co., Wheaton Ill) (Fig 2). The atomizer was modified by inserting a syringe needle (SS 25 gauge 3") into the top of the sprayer to decrease the orifice size. As liquid GB entered through the top of the atomizer, compressed air (30-40 psi) entered through the side to atomize the liquid into fine droplets. Due to the volatility of GB, these droplets quickly evaporated into GB vapor, which were then drawn down through the chamber.

2.4 INHALATION CHAMBER.

GB vapor was monitored in a 750-liter dynamic airflow inhalation chamber located within a 20,000-liter containment chamber. The Rochester style chamber was constructed of stainless steel with Plexiglas windows on each of the six sides. The chamber's negative pressure (~0.25" H_2O) was monitored with a calibrated magnehelix (Dwyer, Michigan City, Ind). Chamber airflow (500 - 650 L/min) was measured at the chamber outlet with a thermo-anemometer (Model 8565, Alnor, Skokie, IL). Monitored environmental parameters included temperature and relative humidity.

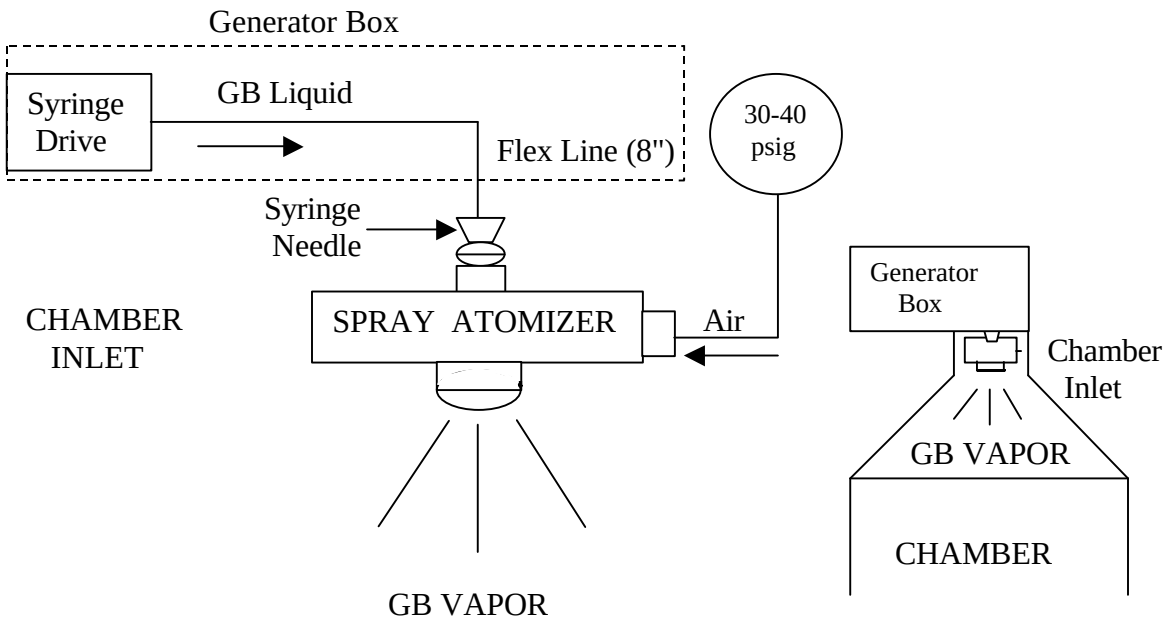


Figure 2. Schematic of spray atomization system.

2.5 SAMPLING SYSTEM

A variety of sampling systems were used to monitor GB vapor in the chamber. The bubbler and sorbent tube systems were quantitative measures of GB while the phosphorus analyzer was used primarily to follow the chamber profile.

All sample flowrates for the bubbler and sorbent tube systems were controlled with calibrated mass flow controllers (Matheson Gas Products, Montgomeryville, PA). Typical flow rates were 0.9 - 1.0 L/min for the bubblers and 100 sccm for the sorbent tubes. Due to solvent (hexane) evaporation during sampling, an in-line charcoal filter was installed between the bubbler and mass flow controller to prevent the cooling effect of the solvent from affecting the mass flow sensor. Flow rates from both systems were verified before and after sampling by temporarily connecting a calibrated flowmeter ("DryCal", Bios Int'l, Pompton Plains, NJ) in-line to the sample stream.

2.5.1 BUBBLER SAMPLING

The concentration of GB in the chamber was determined by collecting chamber air samples into "Edgewood" bubblers containing hexane.[7] During sampling, chamber air was drawn through glass sample lines (.25" o.d.) into paired bubblers (front & rear) at the rate of 0.9 - 1.0 L/min. The collected solvent was diluted to a known volume and injected into a gas chromatograph with flame photometric detection, (GC-FPD) phosphorus mode. External standards (GB/hexane) were injected into the GC-FPD to generate a calibration curve. A linear regression fit ($R^2 = 0.999$) of the standard data was used to compute for GB concentration in the chamber. Instrument parameters for GB analysis by the GC-FPD are listed in Appendix A.

2.5.2 SORBENT TUBE SYSTEM

The automated sorbent tube sampling system (Fig 3) was comprised of four parts: (1) a heated sample transfer line, (2) heated external switching valve, (3) thermal desorption unit and (4) gas

chromatograph. A stainless steel sample line (1/16 in o.d. x .004 in i.d. x 6 ft l) extended from the middle of the chamber to an external sample valve. The sample line was commercially treated with a silica coating (Silicosteel® Restek, Bellefonte, PA) and covered with a heated (60°C) sample transfer line (CMS, Birmingham, Alabama). The combination line coating and heating was to minimize GB adsorption onto sample surfaces. From the transfer line, the sample entered a heated (125°C) 6-port gas switching valve (UWP, Valco Instruments, Houston, Texas). In the by-pass mode, chamber air was continuously drawn through the sample line onto a charcoal vent filter. In the sample mode, the gas sample valve would redirect the chamber air to a 10 mm Tenax TA sorbent tube located in the thermal desorption unit (ACEM-900, Dynatherm Analytical Instruments, Kelton, Pa). Temperature and flow programming within the Dynatherm desorbed GB from the sorbent tube and injected the vapor directly onto the gas chromatograph (GC) for quantitation. Either flame ionization (FID) or flame photometric (FPD) detection could be used depending upon the level of sensitivity required. Instrument parameters for both the GC and the Dynatherm are listed in Appendix A.

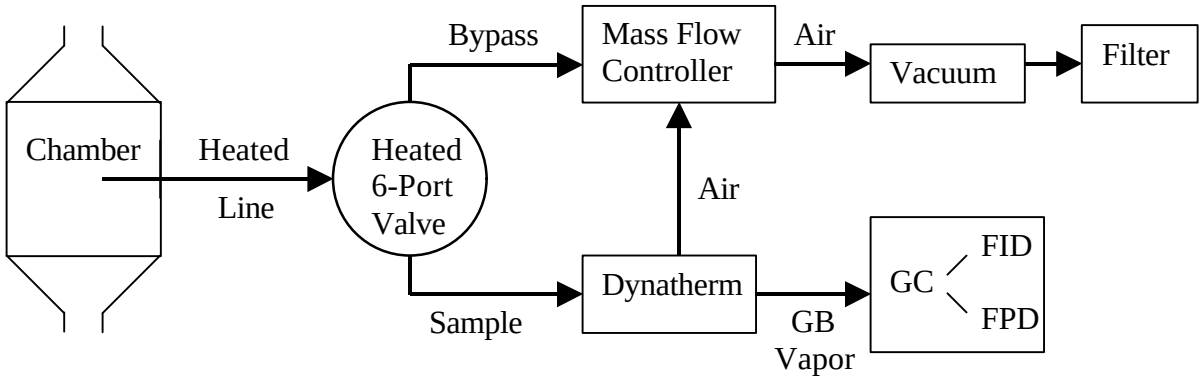


Figure 3. Automated sorbent sampling of GB vapor from the chamber.

Calibration of the sampling and analysis system was conducted by starting the Dynatherm program and injecting external standards (GB/hexane) directly into the inlet of the heated sample line. In this way, injected GB standards were put through the same sampling and analysis stream as were the chamber samples. Standards injected through the sample line as well as directly onto the sorbent tube showed comparable data and demonstrated the integrity of the sample line system. A linear regression fit ($R^2 = 0.999$) of the standard data was used to compute for GB concentration from the chamber samples.

2.5.3 PHOSPHORUS MONITOR (HYFED)

GB levels in the chamber were continuously monitored with a phosphorus analyzer (HYFED, Model PH262, Columbia Scientific, Austin, Texas). The analyzer output was recorded on a strip chart recorder, which showed the rise, equilibrium, and decay of the chamber vapor concentration during each experimental run. In addition, it gave a close approximation of the amount of GB (mg/m^3) in the chamber based on data (bubbler and sorbent tube quantitation with HYFED response) from previous chamber runs.

2.6 CHAMBER RUNS FOR BUBBLER AND SORBENT TUBE COMPARSION

Ten separate chamber runs were conducted to make the bubbler and sorbent tube comparison. Samples were drawn at different chamber concentration's ranging from 2 - 7 mg/m^3 GB. All samples were drawn from the middle of the chamber. Bubbler and sorbent tube samples were drawn after the

chamber attained equilibration (t_{99}) while the HYFED monitored the entire run. Two separate sets of bubblers ran concurrently during each sample collection period while each sorbent tube represented a single measurement. Frequency of sampling for the bubblers was approximately every 20 min for each 60 min run, every 60 min for each 240 min run and every 90 min for each 360 min run. Each bubbler sampling collection period lasted from 8-12 min. Sorbent tube samples were drawn from the chamber approximately every 10 - 15 min with each sample draw lasting 2-3 min.

3. RESULTS

3.1 GB VAPORIZARION SYSTEM

The syringe drive/spray atomization system delivered a constant and stable vapor concentration throughout all testing periods. The system was easy to manipulate and tested effectively at a range of 0.5 to 50 mg/m^3 GB. Chamber profiles from the HYFED phosphorus response showed the stability of the generator over six hour periods. Appendix B illustrates GB vapor (6.0 mg/m^3) stability during a 1 hr chamber run with concurrent sampling via bubblers and sorbent tubes.

3.2 BUBBLER AND SORBENT TUBE COMPARSION

A total of 75 bubbler samples and 145 sorbent tube samples were collected throughout the 10 chamber runs. The mean GB vapor concentration from each sampling method was determined for each run (Table 1). The mean values from each set of runs (60 min, 240 min, and 360 min) were computed and compared against each other using a paired t-test (Table 2). Results showed that the difference of the means between the two sampling techniques were well within the computed 95% confidence interval. Thus, there were no significant differences between the means for the two sampling methods.

TABLE 1. Mean and Variance of GB Vapor Concentrations (mg/m^3) from Bubbler and Sorbent Tubes Obtained during Chamber Runs.

60 Min Chamber Runs	(N)	Bubbler	Sorbent Tube	(N)
1	(4)	5.91 ± 0.23	6.00 ± 0.12	(5)
2	(4)	6.95 ± 0.29	6.98 ± 0.23	(5)
3	(4)	6.55 ± 0.34	6.37 ± 0.16	(5)
240 Min Chamber Runs	**(N)**	**Bubbler**	**Sorbent Tube**	**(N)**
4	(8)	2.12 ± 0.08	2.04 ± 0.04	(12)
5	(8)	3.28 ± 0.09	3.26 ± 0.05	(16)
6	(8)	4.79 ± 0.13	4.87 ± 0.08	(15)
7	(7)	2.64 ± 0.08	2.81 ± 0.10	(15)
360 Min Chamber Runs	**(N)**	**Bubbler**	**Sorbent Tube**	**(N)**
8	(8)	2.99 ± 0.10	2.99 ± 0.09	(25)
9	(8)	2.76 ± 0.19	2.66 ± 0.08	(24)
10	(8)	2.78 ± 0.10	2.77 ± 0.09	(23)

N = Number of Samples

TABLE 3. Paired T-test* of Mean GB Concentrations (mg/m^3) Obtained from each set of Chamber Runs (Bubbler versus Sorbent Tube Samples).

Chamber Run Time	(N)	Bubbler	Sorbent Tube	Difference of Means	95% Confidence Interval
60 Min	3	6.47 ± 0.50	6.45 ± 0.53	-0.02	(-0.37 - 0.33)
240 Min	4	3.21 ± 1.16	3.25 ± 1.20	-0.04	(-0.14 - 0.21)
360 Min	3	2.84 ± 0.13	2.81 ± 0.17	0.03	(-0.37 - 0.33)

*All data was normally distributed with no statistically significant difference between the two sampling methods. Ho = 0.

N = Number of chamber runs per chamber run time (60, 240 & 360 min).

4. DISCUSSION

4.1 VAPORIZATION SYSTEM

The spray nebulization system tested effectively from 0.5 - 50 mg/m^3 GB. A typical chamber run required a syringe drive flow (liquid GB) of 1 - 10 ul/min with a chamber flow of 550 -650 L/min. Adjustments in the syringe drive and chamber flow parameters could probably achieve a lower limit of approximately 0.1 mg/m^3 GB. Testing for subtle clinical effects (i.e. miosis), or at the recommended "TLV-TWA level" of 0.0001 mg/m^3 GB[8] would require the use of a different generator.

4.2 SAMPLING SYSTEMS

Traditionally, discrete sampling for GB vapor has been accomplished through the use of bubblers. Herd *et al*., (1983), and Bartram *et al*., (1988), have evaluated the sampling efficiency of bubblers and impingers to monitor GB vapors.[7,9] Although labor intensive, bubblers have provided a reliable method for the quantitation of GB vapor. Unfortunately, as the GB vapor concentration decreases, the length of sampling time significantly increases. Drawbacks to extended sampling times include increased risk of analyte loss due to evaporation, hydrolysis and breakthrough. In addition, the numbers of samples drawn during an exposure are significantly reduced. An automated solid sorbent system was introduced to offset these drawbacks, especially for use at lower (< 2.0 ug/L) GB concentrations. A comparison of GB concentrations between the bubblers and the sorbent tubes confirmed the performance of the automated approach. A table summary of the advantages and disadvantage of each of the two sampling systems is listed in Appendix C.

Although bubblers can be drawn almost indefinitely, the lower practical limit for bubblers sampling GB in the chamber would probably fall within the range of 0.5 to 2.0 ug/L. Below that range, problems associated with extended sampling times (hydrolysis, breakthrough, sample throughput, solvent evaporation and flow rate adjustments) would occur which may increase error.

Although solid sample tube collection is not a new technology, difficulties may arise when (1) attempting to provide a continuous and deactivated sampling system and (2) quantitation of sample from an automated system. Samples such as GB have a tendency to adsorb onto active metal surfaces. For example, Trurnit *et al*., (1953) reported on the adsorption of GB on the chamber walls.[10] For this reason, a combination of sample line deactivation (silicosteel®) and uniform heating (heated transfer line) were essential to ensure the recovery of the vapor. In addition, the transference of vapor from a chamber

atmosphere to an analytical instrument must follow the ideal gas law (PV = nrt). In other words, for gas sample loop operation, the effects of pressure and temperature that the vapor undergoes during transference must be considered for proper quantitation. In this technique, the flow of GB vapor through the continuous flow sample line was simply diverted to the sorbent tube. Thus, integration of a switching valve with the controlled mass flow meter provided an accurate sample volume.

Future work to detect "low level" GB (< 0.1 - 0.0001 mg/m^3) would include sampling at significantly higher flow rates (2 L/min) and sampling times to increase loading on the Tenax TA. In addition, connection to a GC-FPD detector would increase sensitivity by 2 - 3 orders of magnitude compared to the FID.

4.3 BUBBLER AND SORBENT TUBE COMPARSION

The paired t-test was used to compare the two sampling methods conducted on one sample (GB vapor). In this case, the paired t-test compared the difference between the means of each of the two sampling methods for chamber runs conducted at 60, 240 and 360 min. The null hypothesis (H_o) was that the difference between the two methods equaled zero. Results of the paired t-test failed to reject Ho and concluded that there was no significant difference between the two methods, $p>0.05$.

5. CONCLUSION

A syringe drive coupled to a spray atomizer was effective for the generation of GB vapor in an inhalation chamber at a range of 0.5 to 50 mg/m^3 GB. Investigation into different generation systems will be required for studies below 0.5 mg/m^3 GB.

The automated sorbent tube approach provided a rapid, sensitive methodology for the sampling and quantitation of GB vapor. The system demonstrated an inert sample pathway for continuous sampling from the chamber. A statistical comparison of the bubbler and sorbent tube methods showed that there was no significant difference between the two methods. This study verifies the performance of the Dynatherm-GC sampling and analysis system for future "low-level" GB studies.

REFERENCES

1. Levaggi, D.A., Sampling and Storage of Gases and Vapors in "Methods of Air Sampling and Analysis", Ed. Lodge, J.P., 3rd Edition, Lewis Publishers, Inc. Chelsea, MI., 1989.

2. Abrams, W.C., and Albro, T.G., "Chemical Warfare Agents – Breakdown Products and Precursor Analysis", Presented at the 1993 Scientific Conference on Chemical and Biological Defense Research, Aberdeen Proving Ground, MD.

3. Cullumbine, H., Callaway, S., Ainsworth, M., and R. Lynch. Porton Technical Paper No. 495. The Inhalation Toxicity of GB to Rats, Sheep, Monkeys and Guinea Pigs. 1955. UNCLASSIFIED Report.

4. Barrett, H.M., Porton Technical Paper No. 2756. Studies on the LCt50 of Nerve Gas Vapour in the Rat and the Mouse. 1951 UNCLASSIFIED Report.

5. Callaway, S., and J.W. Blackburn. Porton Technical Paper No. 404. A Comparative Assessment of the Vapour Toxicities of GB, GD, GF, T.2132, T.2137 and T.2146 to Male and Female Rats. Feb 1954. UNCLASSIFIED Report.

6. Mioduszewski, R.J., Manthei, J., Way, R., Burnett, D, Gaviola, B., Muse, W., Anthony, J., Durst, H., Thomson, S., Crouse, C., Crouse, L., Sommerville, D., and R. Crosier. "Estimating Probability of Sarin (GB) Vapor Toxicity in Rats as a Function of Exposure Concentration and Duration", Presented at the 2000 International Chemical Weapons Demilitarisation Conference, May 22-24, The Hague, Netherlands.

7. Bartram, P.W. and Meyers, M.B.,. The Efficiency of Scrubbing CW Agent Vapors in Impingers. CRDEC-TR-88162. August 1988.

8. McNamara, B.P. and F Leitnaker. Toxicological Basis for Controlling Emission of GB into the Environment. Special Publication F.A-SP-100-98, AD 914271L. Medical Research Laboratory, Edgewood Arsenal, Aberdeen Proving Ground, MD. 1971.

9. Herd, R.E., Bouck, J., Kolakowski, J. E., Miskelly, P.P., and Norris, G. Evaluation of the Sampling Efficiency of Beaded Glass Bubblers for Monitoring GB Emissions in Air. ARCSL-TR-82027. May 1983.

10. Trurnit, H.J., Bales, P.D., Esposito, E.J., and Horowitz, P., Comparative Study of GB Inhalation Toxicity on Mice, Rats, Guinea Pigs, Cats, Dogs and Monkeys with Exposure Times Between One Second and Several Minutes. Chemical Corps Medical Laboratories Research Report No. 205. August 1953.

APPENDIX A

GC Parameters for GB Analysis

GC/FPD Operation for Bubblers

Gas chromatograph	Hewlett Packard 6890
Capillary column	DB-5, 30m x 0.53mm i.d., x 1.5 mm film thickness
Injection volume	2 µl
Column flow (He)	13.1 ml/min (velocity 84 cm/sec) (head pres = 9.0 psi)
Septum purge (He)	15 ml/min (9.0 psi)
Detector flow (FPD)	110 ml/min (air); 150 ml/min (hydrogen)
Detector temp (FPD)	250°C
Injector temp	200°C
Injection mode	Splitless, Single taper liner (HP part no 5181-3316)
Inlet Purge	Off Time: 0.00 min; On Time: 0.50 min
Col temperature program	60°C (hold 1 min) to 100°C @ 25°/min (run time: 4 min)

GC/FID Operation for Dynatherm

Same Chromatographic Parameters as above except:

Detector flow (FID)	400 ml/min (air); 30 ml/min (hydrogen)
Detector temp (FID)	250°C

Instrumental Parameters for Thermal Desorption

Model: Dynatherm (ACEM 900)

Temperature/Flow Program:

Tube Desorb	275°C	Tube Heat	3 min
Transfer Line	150°C	Trap Heat	1 min
Trap Desorb	300°C	Tube Dry	1 min
		Tube Cool	1 min
Purge Flow	5 ml/min (He)		
Solid Sorbent	Tenax TA (11.5 cm x 6 mm o.d.)		

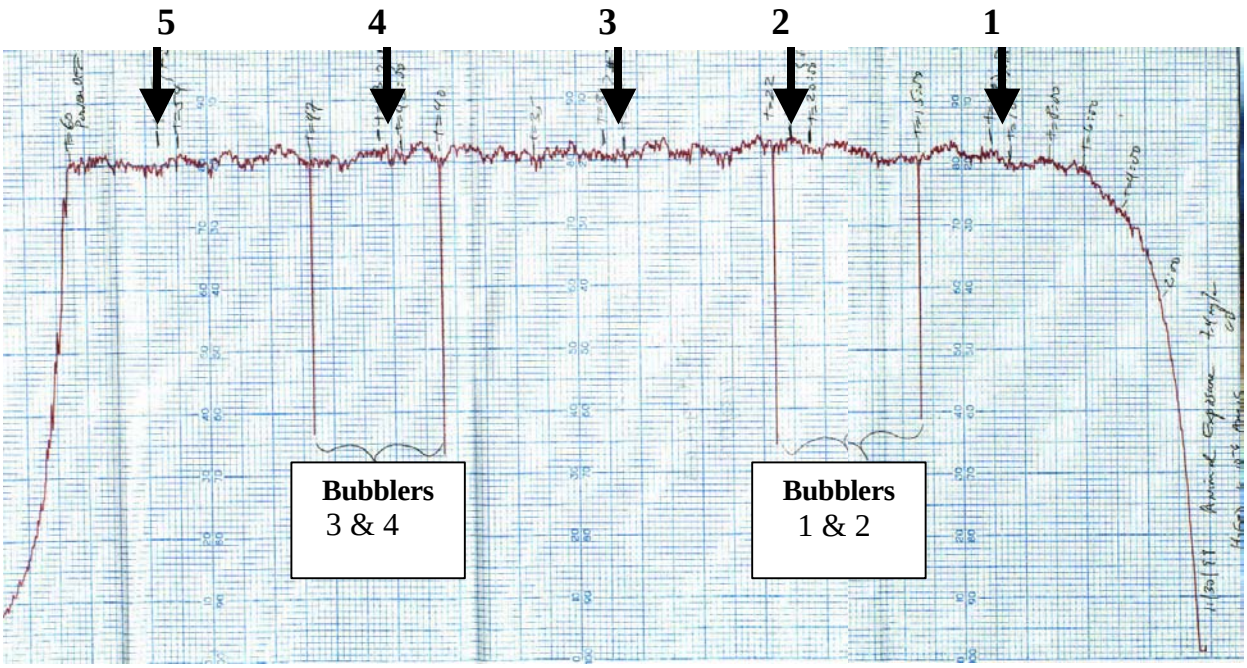
Sample Time:

External Sample	External Standard Calibration through sample line	5-7 min
	External Standard Calibration directly on sorbent tube	0 min
	Chamber Sample	2-3 min

APPENDIX B

GB Vapor Stability During One Hour Chamber Run

Dynatherm Samples (1 – 5)



60 min **45 min** **30 min** **15 min** **0 min**

APPENDIX C

Advantages and Disadvantages of Bubbler vs. Sorbent Tube Sampling

BUBBLERS

Advantages	Disadvantages
1. Reliable method	1. Labor intensive (set-up, sample manipulation connections and leak check).
2. Many previous studies have used bubblers, therefore, provides a basis for comparison studies.	2. Requires front and back bubblers to prevent significant analyte (GB) breakthrough.
	3. Extended sampling draws water into the bubbler solution, which may affect the analyte over time.
	4. Cannot automate
	5. Lower GB concentrations require extended sampling times (iced) which limits the number of samples taken during a run.

SORBENT SAMPLING

Advantages	Disadvantages
1. Continuous sample line from the chamber to the GC. Less chance for leaks or errors.	1. Dust particles in sample line may act as absorption sites. May require sample line deactivation (inject dilute GB) prior to calibration.
2. Not labor intensive (same sorbent tube can be reused, no reconnections or sample manipulations).	
3. System can be easily automated.	
4. Samples can be drawn frequently.	
5. Water vapor does not collect in the sorbent tube.	
6. Larger dynamic range and more sensitive.	
7. Amount of Tenax TA in one tube prevents GB breakthrough.	